

19

Centropolyindans: Benzoannellated Polyquinanes with a Central Carbon Atom

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1. Introduction

There are three principal ways to fuse two five-membered rings: by unifying only one member, two adjacent members, or three consecutive members of each. In organic chemistry, these types of bicyclic structures are well known. In the case of the carbocyclic parent system, cyclopentane (**1**), two rings can be combined to give spiro[4.4]nonane (**2**), bicyclo[3.3]octane (**3**), and bicyclo[2.2.1]heptane (norbornane, **4**). All of them are stable, low-strain molecular systems.

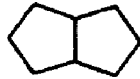
Two stereoisomers of bicyclo[3.3.0]octane (**3**) are known, viz. the *cis* and the *trans* form (**3a** and **3b**). Similar to the stereoisomers of decalin (**5**) and hydrindan (**6**) [1], which do not differ in stability, only **3a** is essentially unstrained; but **3b** is by 27 kJ mol^{-1} less stable than **3a** due to the unfavorable *trans* fusion of the two cyclopentane rings [1, 2]. However, its strain energy is about the same as that of **4** [1, 3]. At this point, the unprepared reader may start wondering about the possibilities of fusing more than two cyclopentane rings in a common polycyclic framework.



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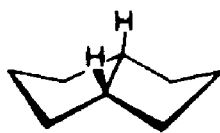
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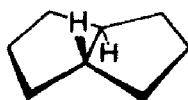
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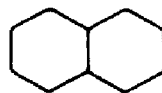
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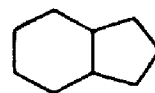
3a



3b



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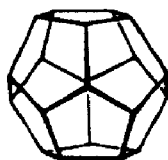


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The chemistry of multiply fused cyclopentane hydrocarbons and their derivatives, termed "polyquinanes" [4–6] has been a very active field of research during the past two decades. In terms of the variety and ease of ring fusion, they indeed represent a borderline class of polycyclic hydrocarbons. Polyquinanes are obviously not as strained as polycyclic small-ring systems (e.g., tetrahedranes, [*l.m.n*]propellanes, cubanes, etc.), yet they are much less known than low-strain polycyclic cyclohexane systems (e.g. [2.2.2]bicyclooctane, twistane, and adamantane) [2, 3]. It appears that the beautiful symmetry of the diamond structure, in particular, has much impacted the understanding of fused cyclohexane hydrocarbons. "Steric fit" and symmetry of multiply fused cyclopentane structures seem less obvious, in part perhaps because of the nonexistence of a diamond modification with fivefold symmetry [7].

Of course, dodecahedrane (7), the "Platonic hydrocarbon" among the polyquinanes, is well established as a low-strain polycyclus with perfect molecular symmetry [8]. Several hexaquinanes, e.g. "[5] peristylane" (8), a "C₁₅-hexaquinane," are subunits of the dodecahedrane sphere [4–6, 9]. But consider *D*₃-trishomocubane (9)[10] and 10, a "C₁₇-hexaquinane," the key polyquinane of this article. Both contain six mutually fused cyclopentane rings as well, but are they "easy-fusing" polyquinane structures?

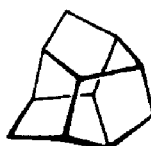
They are! The following sections will concentrate on various polyquinanes related to 10. Special emphasis will be given to the benzoannelated analogues, "centropolyindans," a readily accessible and fascinating class of polycyclic organic molecules.



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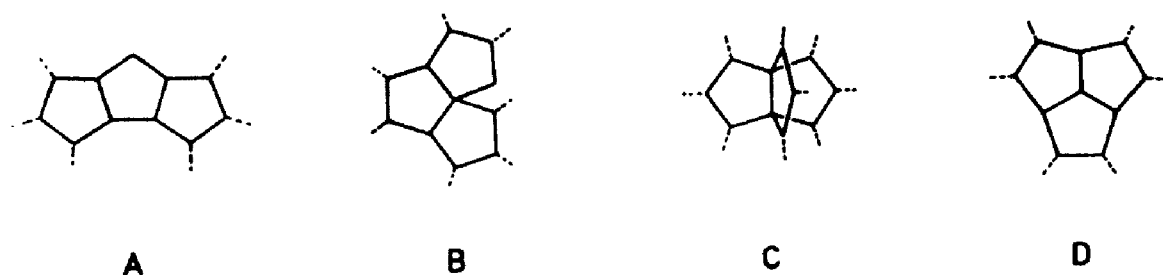


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2. The Principle of Centropolycyclic Ring Fusion

Indeed, there are many different ways to fuse several cyclopentane rings. Linearly (A), angularly (B), and axially (C) annelated skeletons appear in the exciting field of naturally occurring cyclo-

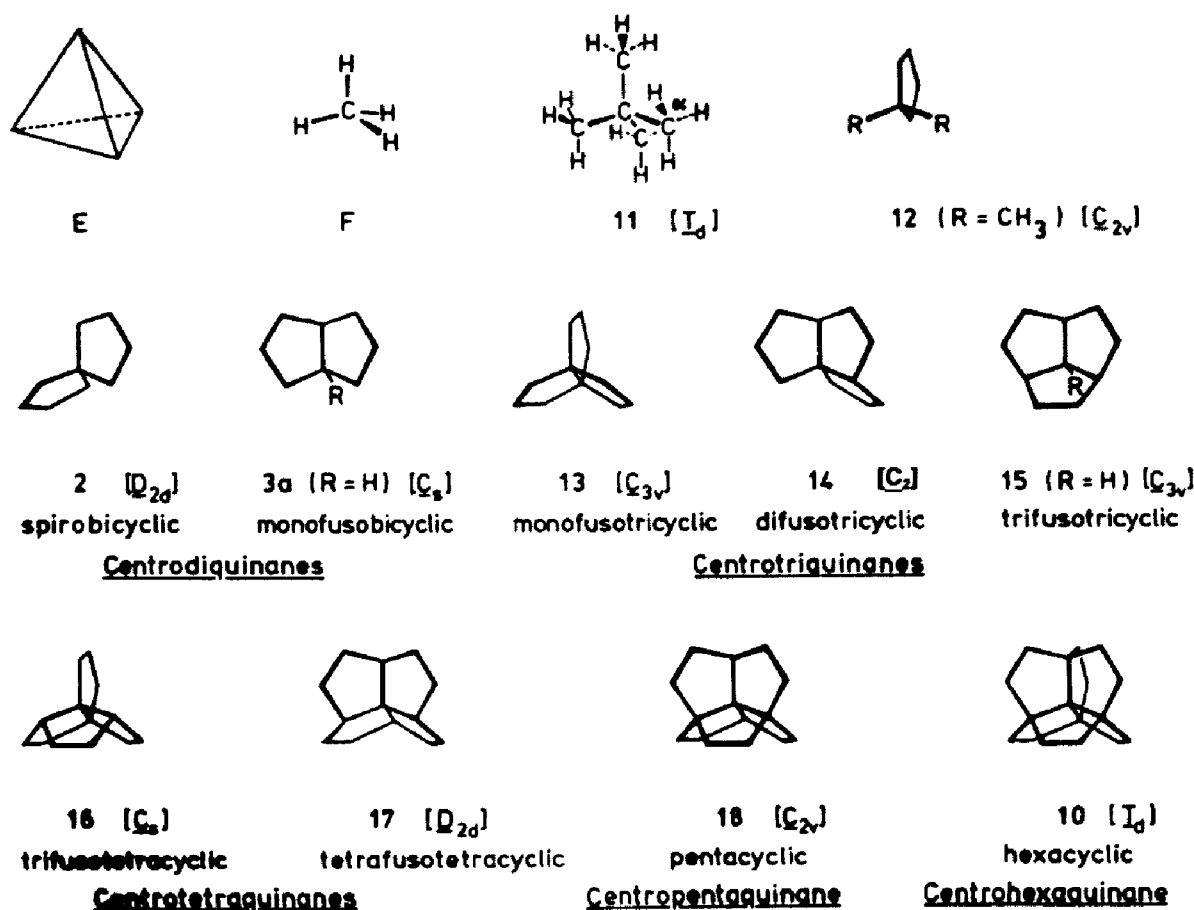
pentanoids[4–6, 11], and the spherical fusion (**D**) is the structural feature of 7–9 and of other unnatural polyquinanes [3–5, 9]. However, another classification of polycyclic structures, proposed a few years ago [7], includes even more complex, three-dimensional cyclopentanoid frameworks in a particularly clear manner. This array of cyclopentane hydrocarbons has been called *centropolyquinanes* [7]. Centrohexaquinane (**10**) is the most perfect and beautiful among the centropolyquinane hydrocarbons. As a particular feature, the atomic connectivity of such centrohexacyclic species is *topologically nonplanar*; that is, their molecular structure cannot be drawn without at least one mutual crossing of atomic bonds [12, 13].



Corresponding to the six edges of a tetrahedron, there is a maximum of six possible bridges between its corners (**E**, Scheme 1)—or between the α substituents of each tetrahedral atomic arrangement derived from methane (**F**). A straightforward way to describe the centrohexacyclic structure of **10** is to bridge *all* pairs of α -C atoms in neopentane (**11**) by ethylene units. Besides the central carbon atom, the four α -C atoms are the only branching points of the polycyclic framework. Branching within the C_2H_4 bridges is not allowed in “regular” centropolyquinanes. All regular centropolyquinanes with less than six rings can be derived from **10**; they are characterized by a central carbon atom that is common to all rings, and by up to four α -C atoms as the only further branching points. Spiro[4.4]nonane (**2**) and *cis*-bicyclo[3.3.0]octane (**3a**) are the simplest centropolyquinanes, viz., *centrodiquinanes*. Norbornane (**4**), however, having a β -branching atom, is not a regular centropolyquinane. The whole array of regular centropolyquinanes with the energetically favorable *cis* fusion of the rings is listed schematically in Scheme 1 [7].

The number of possibilities for connecting a pair of α -C atoms of **11** is equal to that to remove one of the six bridges of **10**. Hence the monocyclo **12** (or **1**) has only one pentacyclic counterpart, *centropentaquinane* (**18**). Twofold bridging gives two *centrodiquinanes* (**2** and **3a**); correspondingly, removal of two bridges from **10** leads to two *centrotetraquinanes* (**16** and **17**). Both pairs of di- and tetraquinanes consist of one isomer with formal D_{2d} symmetry (**2** and **17**) and another with C_s symmetry (**3a** and **16**). Further closure or, respectively, cleavage of a ring with these four polycycles leads to three *centrotriquinanes* (**13–15**), all of them being accessible from the low-symmetry (C_s), but only one (**14**) from the high-symmetry (C_{2d}) congeners.

The nomenclature characterizing the type of centropolycyclic ring fusion denotes the number of fused C–C bonds of the neopentane core. Except



Scheme 1. Regular centropolyquinanes.

for the *spiro*-fused **2**, in which the rings share the central carbon atom only, *mono*-, *di*-, *tri*-, and *tetra*fusocyclic centropolyquinanes can be defined. For example, the three tricycles **13**–**15** can be distinguished as *monofuso*-, *difuso*-, and *trifusocentrotriquinanes*, according to the number of central C–C bonds used for ring junction.

Of course, the principle of centropolycyclic ring fusion is not restricted to centropolyquinanes. Other ring sizes, in particular the cyclohexane analogues (“centropolysexanes” [7]), mixed “centropolycyclanes,” and congeners with remote branching points are possible. The regular centropolyquinanes collected in Scheme 1, however, comprise a particularly concise family of centropolycyclanes.

The geometric conditions for the multiple centroannellation of cyclopentane rings are highly favorable. Different from the cyclohexane analogues, for many of which severe steric interactions have been predicted [7], the much more flexible cyclopentane ring [2] allows the facile fusion of the rings around the central neopentane core. The envelope and half chair conformations of **1** have C–C–C bond angles very close to that of planar **1** (108°) and to those of **11** (109.5°). The steric fit of cyclopentene rings (**19**) [2] and

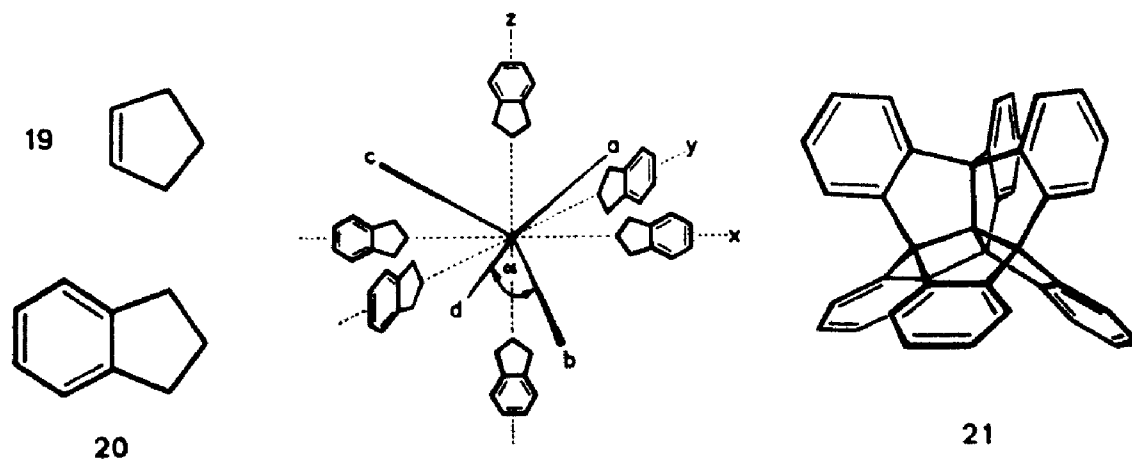
indan units (**20**) should be even better because of less puckering compared to **1**; hence they appear even more promising as bridging entities, in particular for high degrees of annelation (Scheme 2).

From the preparative point of view, indan units are more convenient than nonaromatic C_2 bridges because of their inherent stability and the applicability of the synthetic arsenal of arene chemistry. Indeed, all attempts to synthesize **10** have failed so far. However, structural details of **10** and the corresponding hexaene have been calculated [14]. Most of the *lower* centropolyquinanes are known, but interesting saturated and unsaturated congeners have still eluded their synthesis.

By contrast, the class of benzoannulated centropolyquinanes (centropolyindans) has been completed by synthetic research performed during the recent years in the Bielefeld laboratory [15–21], including the most beautiful among them, “centrohexaindan” (**21**) [19], the first centrohexacyclic and hence topologically nonplanar hydrocarbon. In most cases, surprisingly efficient multiple C–C bond formation approaches have been developed (Section 4).

Centropolyindans and related arenes comprise a promising new group of aromatic hydrocarbons. The arene rings at the periphery of the centropolyquinane were expected to increase the molecular stability, allowing for more strain and a higher degree of unsaturation in the polycyclic core as well as for an increased lifetime of transient, e.g., ionic species. Furthermore, the enlarged “wings” of the rigid centropolyquinane core in centropolyindans and analogues with extended aromatic systems offer π -electron donor sites for complexation with metal fragments in sterically well-defined positions [22–24]. Finally, the intermolecular, solid-state coordination of these polyfused, three-dimensional molecules may be of interest with respect to pinpointed macroscopic properties of organic materials.

Scheme 2. Centrohexaindan (**21**) as viewed by fusing six indan units (**20**) along the Cartesian coordinates (x, y, z) to give four common C–C bonds along the tetrahedral axes $a-d$.



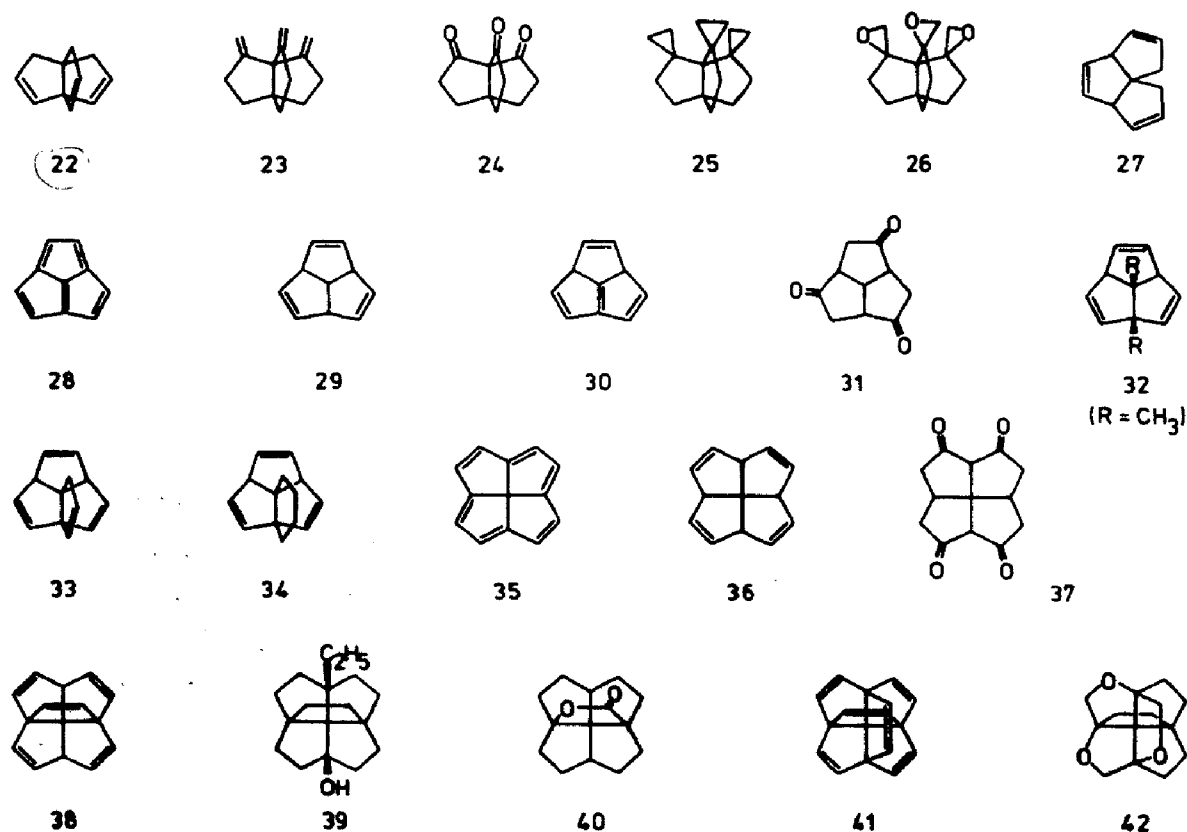
3. Selected Higher Centropolyquinanes

Before discussing the centropolyindans in detail, some few centropolyquinanes will be presented. For comprehensive discussions on polyquinane chemistry, the reader is referred to [4–6, 9, 11]. However, these articles are particularly scarce with respect to benzoannulated centropolyquinanes. Therefore, this section is restricted to *higher* centropolyquinanes, which are of some relevance for the chemistry of the centropolyindans (Scheme 3).

The *monofusocentrotriquinanes* **13** [25] and **23–26**, being prominent members of the well-known class of propellanes [26], have all been synthesized. [3.3.3]propellatriene **22** has apparently not been prepared; but triene **23**, the corresponding trione **24**, and related propellanes have been studied [27]. The trispiro derivatives **25** and **26**, as well as the related mono- and diethers, have been investigated extensively [28–33]. In contrast to the facile conversion of **26** to the isomeric, centrohexacyclic triether **42**, reported in 1981 [28, 29, 33], various attempts to isomerize **25** to the parent hydrocarbon **10** failed [32, 33].

Trifusodiquinane **14** has been prepared recently from a mixture of the C_2 -symmetrical triene **27** and an unsymmetrical isomer [34].

Scheme 3. Centropolyquinane derivatives.



Trifusocentrotriquinanes such as **15** and **28–32** have been investigated extensively. Acepentalene (**28**) is the fully unsaturated and yet unknown hydrocarbon of this series. Its reactivity is predicted to be extremely high [35]. The chemistry of triquinacene (**29**) has been investigated extensively by many groups since its first synthesis by Woodward et al. in 1964 [36; 4–6, 9]. In particular, much work has been invested to achieve the face-to-face dimerization of **29** to dodecahedrane (**7**), including the idea to condense two triketones **31** [37]. Of course, the conversion of **29** to **28** has been pursued. This research led to various metal carbonyl complexes of the corresponding tetraenes, e.g., **30** [35]. Some *centro*-substituted triquinacenes (**32**) have been reported very recently [38].

Trifusocentrotetracyclic structures are very rare. The parent tetraquinane **16** as well as the tetraene **33** are still unknown, but the cyclohexanotriquinacene **34** has been synthesized very recently as the first “regular” trifusocentrotetracyclane [38].

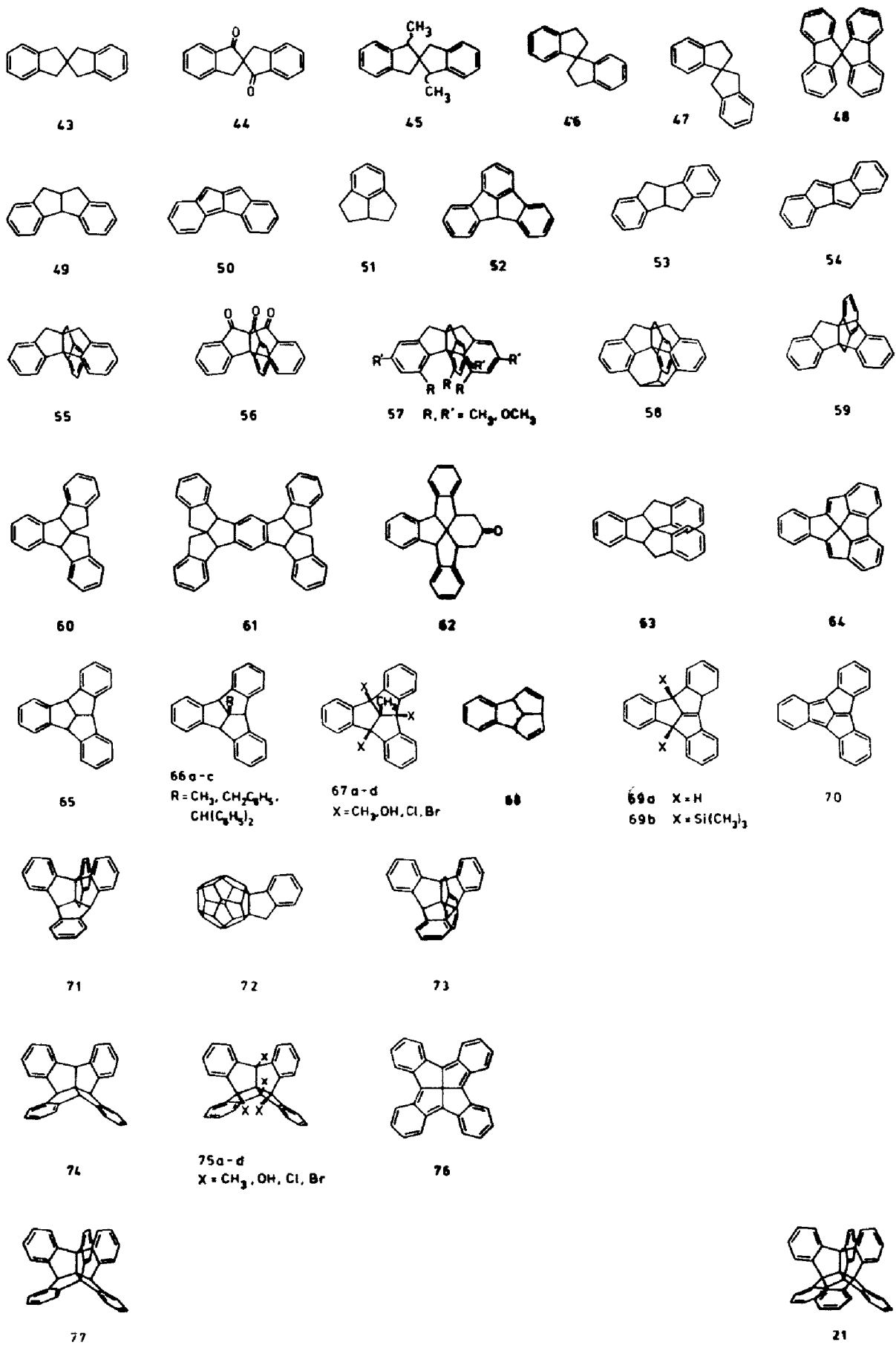
The *tetrafusocentrotetracyclic* congeners have attracted much more interest, being members of the well-recognized class of fenestranes [3, 39–41]. The fully unsaturated hexaene **35** is of high theoretical interest, concerning the planarization of tetracoordinated carbon atoms by embedding it in rigid polycyclic framework. However, **35** seems too strained to be synthetically accessible [39]. The parent all-*cis*-[5.5.5.5]fenestrane (**17**) has been prepared by three independent routes, one of them starting from the tetraketone **37** and involving the tetraene **36** [34].

Centropentaquinane **18** and the pentaene **38** are both unknown. The only known derivative of **18** is the pentacyclic alcohol **39**, which has been obtained in an unsuccessful attempt to convert **25** to **10** [32]. Lactone **40** is a heterocyclic analogue of **18**, from which **17** can be generated by hydrogenolysis [4, 39–41].

The hexaene **41**, like **10**, is still unknown experimentally. However, both of these elusive hydrocarbons have been subject of theoretical studies to predict structural details of the hexacyclic framework [7, 14, 41]. The triether **42** was the first centrohexacyclic, topologically nonplanar molecule reported [28, 29, 33].

4. The Centropolyindans

Benzoannelated centropolyquinanes with various structural features are known. Most of them are collected in Scheme 4. The “regular” centropolyindans **43**, **49**, **55**, **60**, **65**, **71**, **74**, **77** (listed in the left-hand column of Scheme 4) and **21** are all derived from bridging the neopentane core by up to six *ortho*-phenylene units. The whole family of regular centropolyindans is now synthetically accessible, and most members have been reported. Some interesting derivatives are included in Scheme 4. In nonregular centropolyindans, the benzo nuclei are *fused* to the central neo-



Scheme 4. Centropolyindan derivatives.

pentane core (**46–48**, **51–54**, **59**, **63**, **64**, and **73**). Several of them (**47**, **59**, **64**, and **73**) have not been reported yet.

Substituted 2,2'-spirobiindans derived from the parent hydrocarbon **43**, such as the diketone **44** [42] and the 1,1'-dimethyl derivatives **45** [43], are chiral due to their molecular C_2 symmetry and have therefore been a matter of great interest. The same holds for the 1,1'-spirobiindans (**46**) [44, 45], whereas the mixed isomer **47** is not known. A related group of chiral spiroarenes is derived from 9,9'-bifluorene (**48**), the parent compound of the vespirenes [46; 3].

The *fusobiindans* are derived from the regular centropolyindan **49** [47] and its isomer **53** [48]. Detailed studies have been performed concerning the stability and reactivity of corresponding pairs of unsaturated analogues, e.g., **50** and **54**, the latter being the more stable one [49, 50]. There are a few examples of *peri*-benzoannelated diquinanes such as **51** and **52** [3], in which appreciable strain is imposed by the fusion of two vicinal bonds of the benzo nucleus to the nonplanar diquinane moiety. As a consequence, fluoradene (**52**) is much more acidic than triphenylmethane [51].

Triptindan (**55**) is known for more than two decades [52], but various derivatives including **56** and **57** have been synthesized only recently [17, 18, 21], and a new synthetic access to **55** has been found. The three *endo*-substituents in **57** and related triptindans markedly increase the axial torsion of the propellane skeleton. The *endo*-capped derivative **58** represents a challenging goal because of its fixed bullvalene-type structure. **59**, a non-regularly fused centropolyindan, is not known either.

A very efficient cyclization route has been found to synthesize the angular triindan **60** [15]. Other *difusocentropolyindans* such as **61** [21] and **62** [16] can be prepared by using the same approach. Chiroptical properties and the absolute configuration of **62** and other benzoannelated fenestranes have been determined as well [21]. **63**, an isomer of **60**, was synthesized in an attempt to generate **64** and to study the geometry at the central carbon atom of this elusive, highly strained fenestrane [53].

The *trifuso* framework of tribenzotriquinacene **65** [20, 21] and various *centro* and bridgehead substituted derivatives (**66** and **67**) [15, 21] provides a very rigid framework with a C_{3v} symmetrical "concave" *endo* face bearing three isolated benzenoid π -systems. *Monobenzotriquinacene* (**68**) has also been described [5]. **65** and even **66** can be converted to **69b**, a derivative of the strained, still unknown, tribenzodihydroacepentalene **69a** [20, 23]. The dianion of tribenzoacepentalene (**70**) is formed as an intermediate, suggesting the possibility of generating this elusive, strained polyene [20].

Trifusocentrotetraindan (**71**) has been prepared very recently [21]. The only other benzoannelated *trifusocentropolyquinane* reported is indano-dodecahedrane **72** [4]. **73**, the highest unregular centropolyindan, is still unknown.

"Fenestrindan" (**74**) [16] and other *tetrafusocentrotetraindans* [21] have been studied in greater detail because of the possibility of pinpointed mod-

eration of the geometry of tetracoordinated central carbon atom by the [5.5.5.5]fenestrane skeleton [41]. In this context, various bridgehead-substituted fenestrindans (**75**) have been studied [21]. One of the most challenging synthetic targets in this series is "fenestrindene" (**76**), the fully unsaturated congener of **74**.

Centropentaindan (**77**) has been prepared very recently as the last member of the family of regular centropolyindans [21].

Centrohexaindan (**21**) [19] certainly has the most beautiful structure of all centropolyindans since it comprises all of the other regular congeners in its molecular framework. Two efficient, independent syntheses have been developed (Section 4.1.4).

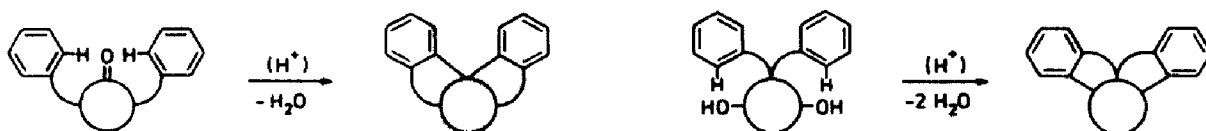
4.1. The Synthesis of the Higher Centropolyindans

4.1.1. The Cyclization Principle The synthesis of the centropolyindans is based on readily available aromatic substrates. Suitably substituted 1-indanones and 1,3-indandiones are used as starting materials, which, in most cases after reduction to the corresponding alcohols, are subjected to acid-catalyzed cyclization with concomitant elimination of water. The two principal cyclodehydration steps are generalized in Scheme 5. Although being the intramolecular variant of one of the classic of electrophilic aromatic substitution reactions (Friedel–Crafts alkylation), this approach proved extremely useful for ring closure in the centropolyindan series. The twofold C–C coupling steps performed in most cases renders most of the preparations highly efficient. One of the two syntheses of centrohexaindan (**21**) involves even a triple cyclodehydration reaction as the final step.

In the beginning of our synthetic efforts, the annelation of up to six benzo bridges around the neopentane core seemed hopeless. Several unfavorable trends had to be considered. (1) The steric crowding of organic ligands at the central, quaternary carbon atom, (2) electrofugic properties of benzylic groups emerging in cationic intermediates, (3) ring cleavage of 1,3-indandiols as substrates for cyclodehydration (Grob-type fragmentation), and (4) steric orientation of the phenyl groups to be cyclized. Indeed, various fragmentation products were obtained in earlier attempts [15, 21].

4.1.2. Triptindan, Difusocentrotriindans, and Tribenzotriquinacenes Thompson's original synthesis of triptindan (**55**) [52] has been simplified considerably [21]. By starting from 1,3-indandione (**78**), it can

Scheme 5.

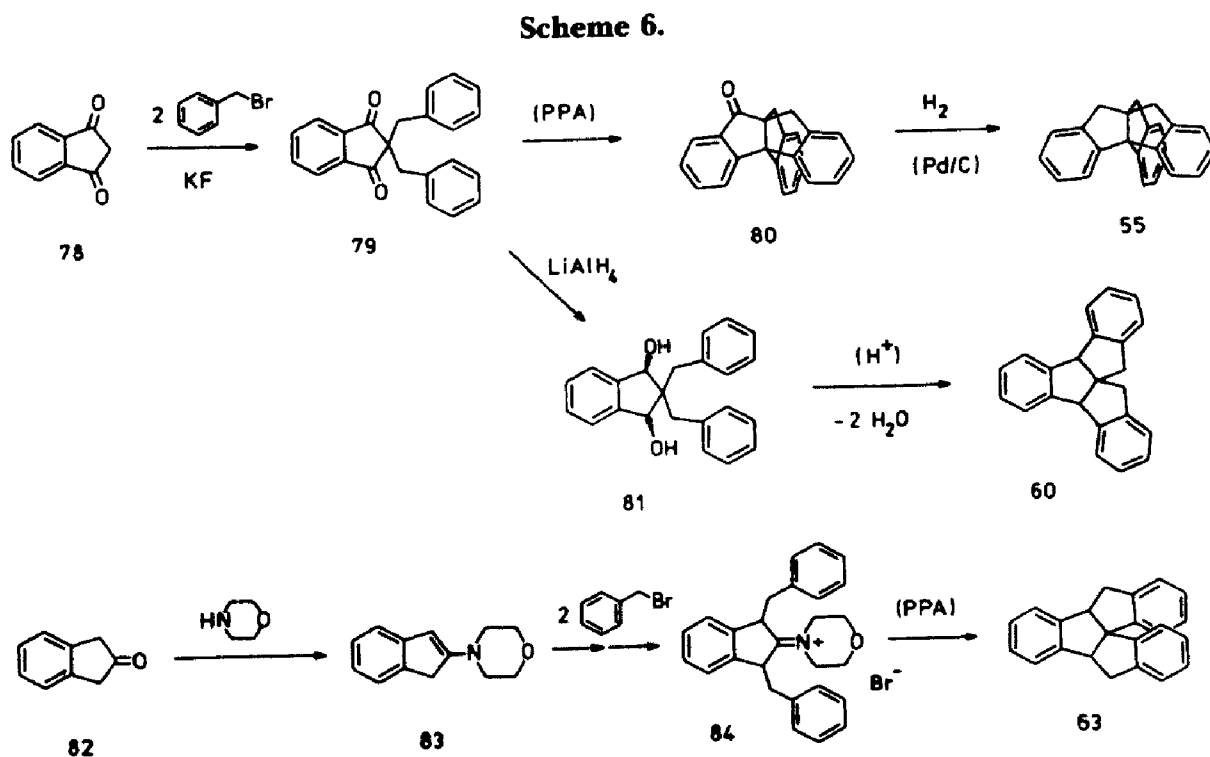


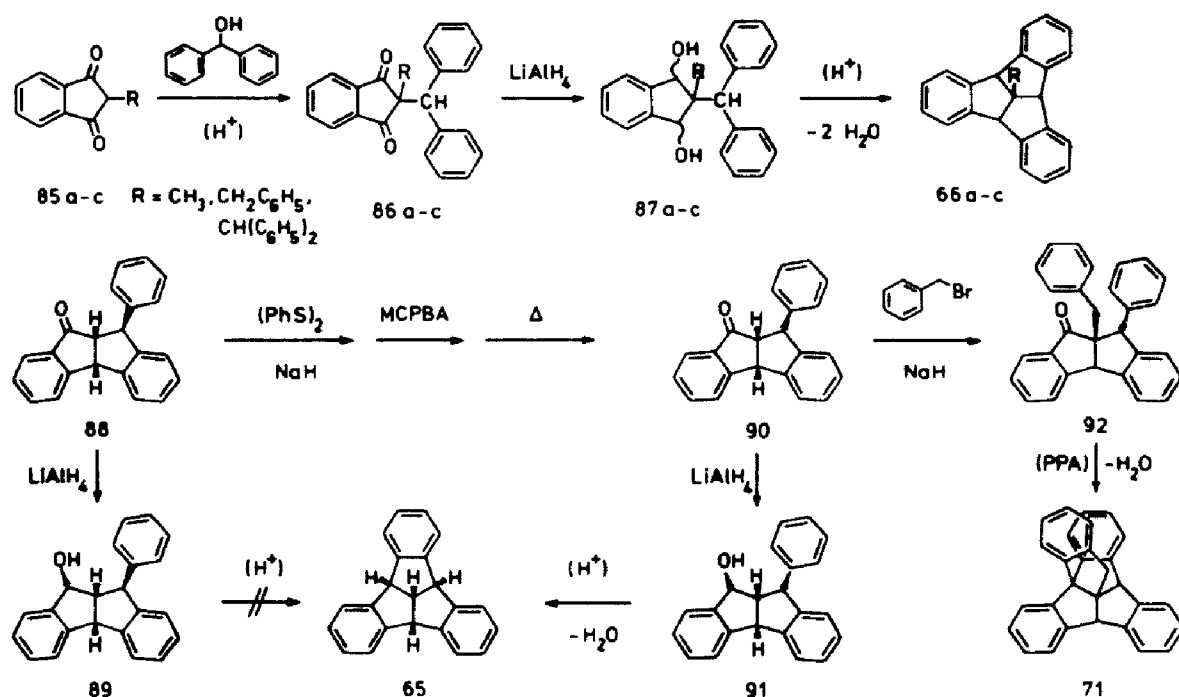
be prepared in three steps with an overall yield of $\approx 60\%$ (Scheme 6). The *difuso* isomer **60** is obtained after reduction of **79** to the 1,3-indandiol **81** and double cyclodehydration in 85% overall yield [15]. Ten Hoeve and Wynberg prepared the nonregular centrotriindan **63** in $\sim 40\%$ overall yield starting from 2-indanone (**82**). Again, a double cyclization was performed in the last step (**84** \rightarrow **63**).

Centro-substituted tribenzotriquinacenes **66a–66c** can be synthesized from 2-substituted 2-benzhydryl-1,3-indandiones **86a–86c** via the 1,3-indandiols **87a–87c** (Scheme 7) [15, 21]. The twofold cyclodehydration of the benzhydryl group can take place only if the first cyclization leads to an *endo*-oriented intermediate (cf. **89/91**).

Some decades ago, the parent tribenzotriquinacene (**64**) was already considered a possible cyclodehydration product of epimeric diindan alcohols such as **89** [49]. However, the *exo*-orientation of the phenyl groups in **88** and **89**, realized later [54], precluded the cyclodehydration. Therefore, a three-step dehydrogenation–rehydrogenation procedure was developed to give the *endo*-phenyl stereoisomer **90**, which after reduction to **91** affords **65** in good yield (Scheme 7) [20]. This synthesis represents one of the few cases in which a stepwise cyclization procedure was found to be superior to the double cyclodehydration strategy.

4.1.3. *The Centrotetraindans and Centropentaindan* Trifuso-centrotetraindan (**71**, Scheme 7) has been prepared in a double cyclization step, after introducing a benzyl group in ketone **90** to give **92**. Similar to





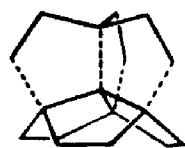
Scheme 7.

91, the *endo*-phenyl group in **92** is fixed in a very favorable orientation, and the benzyl group is probably cyclized *after* the phenyl group [21].

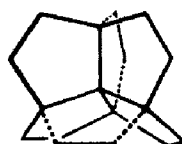
The double cyclodehydration strategy proved extremely convenient as an entry to the benzoannulated fenestranes (Scheme 8), including fenestrindan (**74**) [16]. The *trans*-diphenyl-spirotriketone **93** [55] provided ideal stereochemical conditions for double cyclodehydration after conversion to triol **94**. The [6.5.5.5]fenestranes **95** and **62** are obtained in ~ 50% overall yield. Some further transformations lead to tribenzo[5.5.5.5]fenestrene **96** and fenestrindan **74** [16].

Centropentaindan (**77**) is still the hardest to make of all centropolyindans. Up to now, a maximum of 9% yield has been achieved by *cyclodehydrogenation* of the benzhydryltribenzotriquinacene **66c** (Scheme 8) [21].

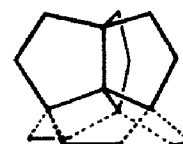
4.1.4. Centrohexaindan The synthesis of centrohexaindan (**21**) deserves a separate section. Two synthetic routes have been developed. It is interesting to note that they represent two of the three strategies (G–I) envisaged by Simmons [33] for the synthesis of the elusive centrohexaquinane (**10**).



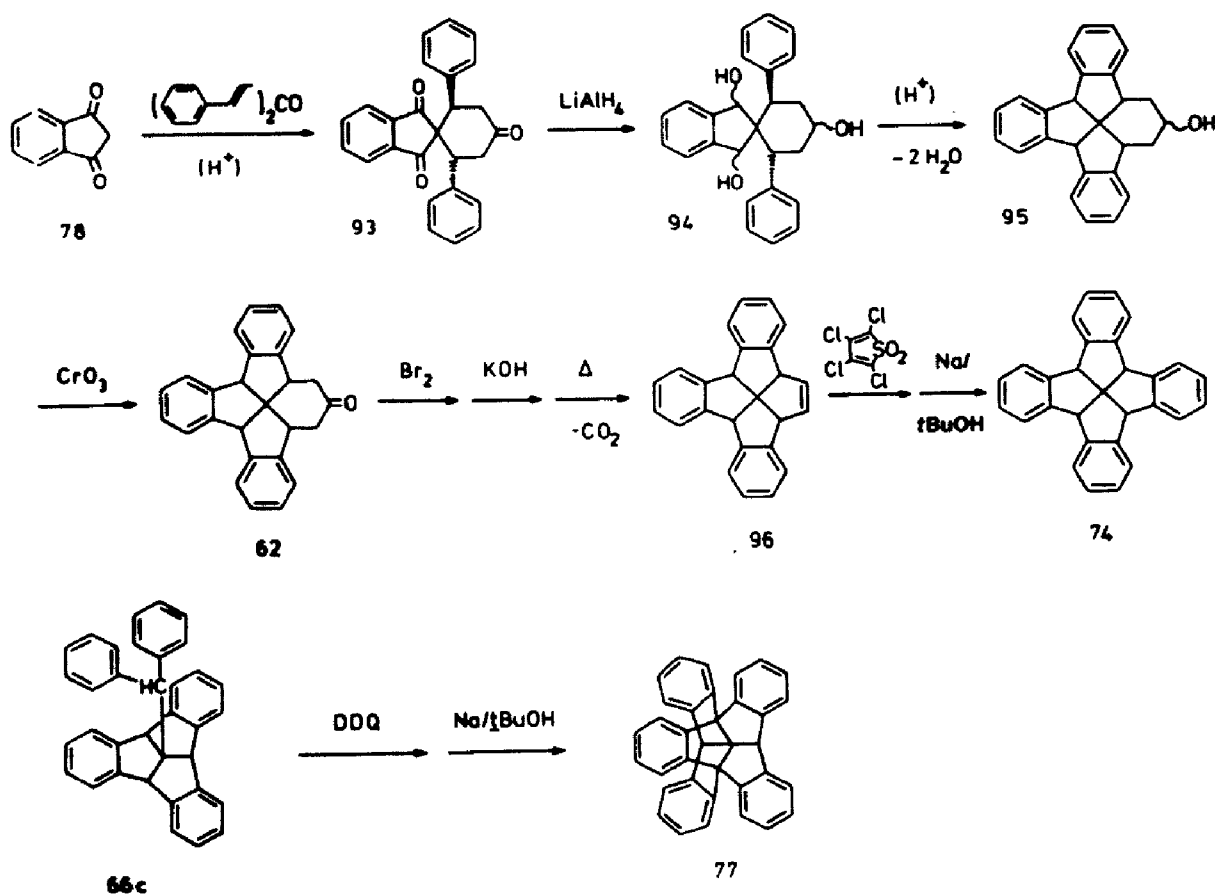
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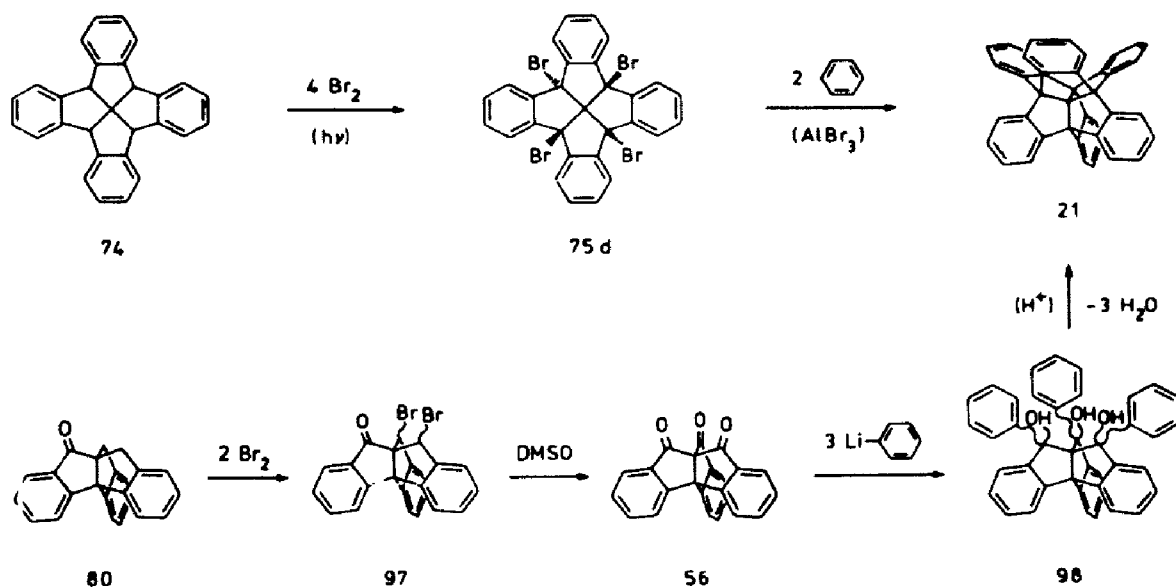
Scheme 8.

The first synthesis of **21** (Scheme 9) [19] was based on fenestrindan **74**. Its tetracyclic framework is particularly resistant to fragmentation. With regard to steric crowding in **75d**, the fourfold bridgehead bromination is surprisingly facile, and the readily occurring incorporation of two further benzene rings by fourfold C–C bond formation, corresponding to approach **H**, is even more so. In total, the synthesis of **21** comprises eleven steps from **78**, with an overall yield of $\sim 4\%$.

The very recently accomplished second synthesis of **21** [21] is much shorter, yielding the hexacyclus in only six steps from **78** with $\sim 35\%$ overall yield. Triptindantrione (**56**) is produced in two steps from the monoketone **80**. Surprisingly again, it adds three phenyl groups to give the triol **98**, which yields **21** on threefold cyclodehydration. This synthesis, corresponding to Simmons' approach **I**, is particularly straightforward. It represents the first successful transformation of a [3.3.3]propellane to a centrohexasquinane.

4.2. Some Structural Aspects

Owing to their high molecular symmetry, it is interesting to study structural properties of the now completely accessible group of centropolyindans, both in terms of intra- and intermolecular interactions.



Scheme 9.

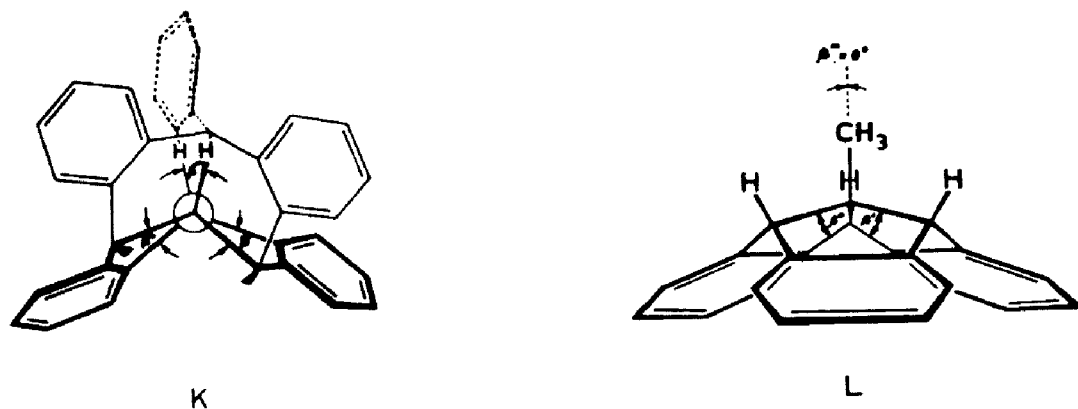
At present, spectroscopic and solid-state investigations are underway, a few results of which are discussed in this section.

In saturated centropolyquinanes, even in **10**, a limited conformational flexibility is preserved [2, 6, 14]. Unsaturated derivatives, such as **24** [56], **37** [25], **41** [14], and the centropolyindans are more rigid, and the remaining flexibility depends markedly on the degree and way of ring fusion.

Spirobiindan (**43**) adopts four equivalent ground-state conformations, according to the combination of two envelope forms [43]. Solid-state *fuso*-diindan **49** exists in two equivalent conformations, which equilibrate in solution to give a time-averaged C_s symmetric molecule. The X-ray structure of **49** [47] exhibits dihedral ("torsional") angles $\beta' = 14.8^\circ$, $\beta'' = 16.5^\circ$, and $\beta''' = 17.1^\circ$ at the central C–C bond (**K**, Scheme 10). Similar conformations have been found for various chromium tricarbonyl complexes of **49** and **53** [57].

Triptindan (**55**) exists in two equivalent C_3 symmetric rotamers with, as compared to **49**, increased torsional angles $\beta' (= \beta'' = \beta''') = 23.8 \pm 0.4^\circ$. (**K**, Scheme 10) in the solid state [21]. According to force-field calculations, the torsion is considerably increased by the interaction of three *endo* substituents (e.g., **57**) [18]. X-Ray structural analysis of the *difuso* isomer **60** reveals a similar but slightly unsymmetric torsion of the two central C–C bonds ($22.0 \leq \beta \leq 24.5^\circ$) [21].

By contrast, the trifuso isomer **66a** exists as a single C_{3v} symmetrical conformer. The orientation of the central methyl group is perfectly eclipsed ($\beta''' = 0^\circ$, **L** in Scheme 10), and the six dihedral C–C bond angles within the indan units (e.g., β' and β'') are only 3.6° . Owing to its pronounced cup-like shape, **66a** forms intermolecular stacks along the molecular axis of symmetry with an intermolecular distance of 6.0 \AA [21].



Scheme 10. Conformational torsion of some centropolyindans. **K**, Newman projections of *fusodiindan* **49** (in bold), *triptindan* **55** (add dotted line indan unit), and *fenestrindan* **74** (add, instead, full line indan units). **L**, Projection, inclined to the back, of *trifusotriindan* **66a**.

In turn, solid-state *fenestrindan* (**74**) [16] exists in two equivalent conformations with S_4 symmetry and two sets of four equivalent central dihedral angles $\beta' = 19.6 \pm 1.0^\circ$ and $\beta'' = 21.1 \pm 0.9^\circ$ (**K**, Scheme 10). A similar but unsymmetrical torsion has been found for **37** [25]. At room temperature, solutions of **74** show rapid equilibration of the rotamers. Similar to **57**, repulsion of the pairs of bridgehead substituents (**75a–75d**) increases the internal torsion. Thus, extreme torsion of the central C–C bonds ($23 \leq \beta' \leq 28^\circ$ and $25 \leq \beta'' \leq 33^\circ$) has been estimated from force-field calculations, and solutions of **75c** and **75d** exhibit static behavior of the conformers on the NMR time scale [21].

Obviously, all centropolyindans without *trifuso* junction (**43**, **49**, **55**, **60**, and **74**) exist in at least two equivalent rotamers with mean torsional angles in the order of $15\text{--}30^\circ$. Conversely, **71** and **77** are predicted to exist in one rotamer only due to the steric locking of the *trifuso* arrangement of (at least) three indan units, as has been found for **66a**. Of course, the X-ray structural analysis of *centrohexaindan* (**21**) gives the final answer: It shows that, in fact, the four central C–C bonds in this fourfold tribenzotriquinacene are perfectly eclipsed with all central dihedral angles $\beta = 0^\circ$. The two indan units of the three 2,2'-spirobiindan systems are exactly orthogonal to each other, and the dihedral angle between the benzo rings of each of the 12 *fusodiindan* subunits is 120° . Overall, as has been predicted for the hexaene **41** [14], the molecular symmetry of *centrohexaindan* is perfectly tetrahedral (T_d).

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REFERENCES

1. N. L. Allinger, "Conformational analysis. 130. MM2. A hydrocarbon force field utilizing V_1 and V_2 torsional terms," *J. Am. Chem. Soc.*, **99**, 8127–8134 (1977).
2. U. Burkert and N. L. Allinger, *Molecular Mechanics*. American Chemical Society, Washington, D.C., 1982.
3. A. Greenberg and J. F. Liebman, *Strained Organic Molecules*. Academic Press, New York, 1978.
4. L. A. Paquette and A. M. Doherty, *Polyquinane Chemistry, Synthesis and Reactions*. Springer-Verlag, Berlin, 1987.
5. L. A. Paquette, "The development of polyquinane chemistry," *Top. Curr. Chem.*, **79**, 41–165 (1979).
6. L. A. Paquette, "Recent synthetic developments in polyquinane chemistry," *Top. Curr. Chem.*, **119**, 1–163 (1984).
7. P. Gund and T. M. Gund, "How many rings can share a quarternary atom?," *J. Am. Chem. Soc.*, **103**, 4458–4465 (1981).
8. J. C. Gallucci, C. W. Doecke, and L. A. Paquette, "X-ray structure analysis of the pentagonal dodehedrane hydrocarbon (CH)₂₀," *J. Am. Chem. Soc.*, **108**, 1343–1344 (1986).
9. P. E. Eaton, "Towards dodecahedrane," *Tetrahedron*, **35**, 2189–2223 (1979).
10. H. Müller, J.-P. Melder, W.-D. Fessner, D. Hunkler, H. Fritz, and H. Prinzbach, "Funktionalisierte, enantiomerenreine [2.1.1]-, [2.2.1]- und [2.2.2]Triblatane," *Angew. Chem.*, **100**, 1140–1143 (1988); *Angew. Chem. Int. Ed. Engl.*, **27**, 1103–1106 (1988).
11. B. M. Trost, "Cyclopentanoids: A challenge for new methodology," *Chem. Soc. Rev.*, **11**, 141–170 (1982).
12. A. T. Balaban (ed.), *Chemical Applications of Graph Theory*. Academic Press, London, 1976.
13. J. Simon, "A topological approach to the stereochemistry of nonrigid molecules," in *Graph Theory and Topology in Chemistry*, R. B. King and D. H. Rouvray (eds.). Elsevier, Amsterdam, 1987, pp. 43–75.
14. O. Ermer, *Aspekte von Kraftfeldrechnungen*. Wolfgang Baur Verlag, München, 1981.
15. D. Kuck, "Ein einfacher Zugang zu benzoanellierten Centropolyquinanen," *Angew. Chem.*, **96**, 515–516 (1984); *Angew. Chem. Int. Ed. Engl.*, **23**, 508–509 (1984).

16. D. Kuck and H. Bögge, "Benzoannelated centropolyquinanes. 2. *All-cis*-tetra-benzotetracyclo[5.5.1.0^{4,13}.0^{10,13}][tridecane, 'Fenestrindan'," *J. Am. Chem. Soc.*, **108**, 8107–8109 (1986).
17. D. Kuck, B. Paisdor, and H.-F. Grützmacher, "Benzoanellierte Centropolyquinane, 3. Synthese mehrfach substituierter Triptindane (9*H*, 10*H*-4b, 9a-([1,2]Benzenomethano)indeno[1,2-*a*]indene) mit drei Substituenten in der Molekülhöhlung," *Chem. Ber.*, **120**, 589–595 (1987).
18. B. Paisdor, H.-F. Grützmacher, and D. Kuck, "Benzoanellierte Centropolyquinane, 4. Sterische Effekte in mehrfach substituierten Triptindanen (9*H*, 10*H*-4b, 9a-([1,2]Benzenomethano)indeno-[1,2-*a*]indenen)," *Chem. Ber.*, **121**, 1307–1313 (1988).
19. D. Kuck and A. Schuster, "Die Synthese von Centrohexasindan—dem ersten Kohlenwasserstoff mit topologisch nicht-planarer Molekülstruktur," *Angew. Chem.*, **100**, 1222–1224 (1988); *Angew. Chem. Int. Ed. Engl.*, **27**, 1192–1194 (1988).
20. D. Kuck, A. Schuster, B. Ohlhorst, V. Sinnwell, and A. de Meijere, "Auf dem Wege zum Tribenzoaceptalen: Tribenzotriquinacen, Tribenzodihydroaceptalendiid und Tribenzoaceptalen-Radikalanion," *Angew. Chem.*, **101**, 626–628 (1989); *Angew. Chem. Int. Ed. Engl.*, **28**, 595–597 (1989).
21. D. Kuck et al., in preparation.
22. A. Cecon, A. Gambaro, F. Manoli, A. Venzo, G. Valle, D. Kuck, and T. E. Bitterwolf, submitted.
23. B. Ohlhorst, "Zur Chemie des Dihydroaceptalen-systems: Dianionen, Bistrimethylsilylderivate und Dimere," Doctoral Thesis, University of Hamburg, 1989.
24. J. Siegel, private communication, 1988.
25. R. Mitschka, J. Oehldrich, K. Takahashi, J. M. Cook, U. Weiss, and J. V. Silverton, "General approach for the synthesis of polyquinanes. Facile generation of molecular complexity via reaction of 1,2-dicarbonyl compounds with dimethyl 3-ketoglutarate," *Tetrahedron*, **37**, 4521–4542 (1981).
26. D. Ginsburg, *Propellanes, Structures and Reactions*. Verlag Chemie, Weinheim, 1975.
27. R. Gleiter, E. Litterst, and J. Drouin, "Interactions in 2,8,9-trifunctional [3.3.3]propellanes," *Chem. Ber.*, **121**, 923–926 (1988).
28. H. E. Simmons, III, and J. E. Maggio, "Synthesis of the first topologically non-planar molecule," *Tetrahedron Lett.*, **22**, 287–290 (1981).
29. L. A. Paquette and M. Vazeux, "Threefold transannular epoxide cyclization. Synthesis of a heterocyclic C₁₇-hexaquinane," *Tetrahedron Lett.*, **22**, 291–294 (1981).
30. J. E. Maggio and H. E. Simmons, III, "Trispiro[tricyclo-[3.3.3.0^{1,5}]undecane-2,1':8,1":9,1"-tris-[cyclopropane]], a chiral fluxional hydrocarbon," *J. Am. Chem. Soc.*, **103**, 1579–1581 (1981).
31. S. A. Benner, J. E. Maggio, and H. E. Simmons, III, "Rearrangement of a geometrically restricted triepoxide to the first topologically nonplanar molecule: A reaction path elucidated by using oxygen isotope effects on carbon-13 chemical shifts," *J. Am. Chem. Soc.*, **103**, 1581–1582 (1981).

32. L. A. Paquette, R. V. Williams, M. Vazeux, and A. R. Browne, "Factors conducive to the cascade rearrangement of sterically congested and geometrically restricted three-membered rings. Facile synthesis of a topologically nonplanar heterocycle," *J. Org. Soc.*, **49**, 2194–2197 (1984).
33. H. E. Simmons, III, "The synthesis, structure, and reactions of some theoretically interesting propellanes: The synthesis of the first topologically non-planar organic molecule," PhD Thesis, Harvard University, 1980.
34. M. Venkatachalam, M. N. Desphande, M. Jawdosiuk, G. Kubiak, S. Wehrli, J. M. Cook, and U. Weiss, "General approach for the synthesis of polyquinenes," *Tetrahedron*, **42**, 1597–1605 (1986).
35. H. Butenschön and A. de Meijere, "The first carbonyl iron complexes with dihydroacepentalene ligands," *Tetrahedron*, **42**, 1721–1729 (1986).
36. R. B. Woodward, T. Fukunaga, and R. C. Kelly, "Triquinacene," *J. Am. Chem. Soc.*, **86**, 3162–3164 (1964).
37. E. Carceller, M. L. García, A. Moyano, M. A. Pericàs, and F. Serratosa, "Synthesis of triquinacene derivatives. New approach towards the synthesis of dodecahedrane," *Tetrahedron*, **42**, 1831–1839 (1986).
38. A. K. Gupta, G. S. Lannoye, G. Kubiak, J. Schkeryantz, S. Wehrli, and J. M. Cook, "General approach to the synthesis of polyquinenes. 8. Synthesis of triquinacene, 1,10-dimethyltriquinacene, and 1,10-cyclohexanotriquinacene," *J. Am. Chem. Soc.*, **111**, 2169–2179 (1989).
39. B. V. Rao and W. C. Agosta, "Fenestranes and the flattening of tetrahedral carbon," *Chem. Rev.*, **87**, 399–410 (1987).
40. K. Krohn, "Fenestrane—Blick auf strukturelle Pathologien," *Nachr. Chem. Techn. Lab.*, **35**, 264–266 (1987).
41. W. Luef and R. Keese, "Angular distortions at tetracoordinate carbon. Planoid distortions in α,α' -bridged spiro[4.4]nonanes and [5.5.5]fenestranes," *Helv. Chim. Acta*, **70**, 543–553 (1987).
42. H. Falk, W. Fröstl, und K. Schlögl, "Darstellung, absolute Konfiguration und optische Reinheit von 2,2'-Spirobiindan-1,1'-dion," *Monatsh. Chem.*, **105**, 574–597 (1974).
43. P. Lemmen and I. Ugi, "The chiroptic properties of the diastereomeric 1,1'-dimethyl-2,2'-spirobiindans—a comparative study," *Chem. Scr.*, **27**, 297–301 (1987).
44. J. H. Brewster and R. T. Prudence, "Absolute configuration and chiroptical properties of optically active 1,1'-spirobiindan, 1,1'-spirobiindene, and 1,1'-spirobiindanone," *J. Am. Chem. Soc.*, **95**, 1217–1229 (1973).
45. R. K. Hill and D. A. Cullison, "Dissymmetric spirans. II. Absolute configuration of 1,1'-spirobiindene and related compounds," *J. Am. Chem. Soc.*, **95**, 1229–1239 (1973).
46. G. Haas and V. Prelog, "Optisch aktive 9,9'-Spirobifluoren-Derivate," *Helv. Chim. Acta*, **52**, 1202–1218 (1969).
47. J. M. M. Smits, J. H. Noordik, P. T. Beurskens, W. H. Laarhoven, and F. A. T. Lijten, "Crystal and molecular structure of *cis*-dibenzobicyclo[3.3.0]octa-2,7-diene, C₁₆H₁₄," *J. Cryst. Spectrosc. Res.*, **16**, 23–29 (1986).

48. R. S. D. Mittal, S. C. Sethi, and Sukh Dev, "Azulenes and related substances—XV. Azuleno[2,1-*a*]azulene: Reaction of 3,6,7,8-tetrahydrodibenzopentalene with diazomethane; synthesis of 11*H*-indeno[2,1-*a*]azulene," *Tetrahedron*, **29**, 1321–1325 (1973).
49. W. Baker, J. F. W. McOmie, S. D. Parfitt, and D. A. M. Watkins, "Attempts to prepare new aromatic systems. Part VI. 1:2-5:6-Dibenzopentalene and derivatives," *J. Chem. Soc.*, 4026–4037 (1957).
50. M. Randić, "Aromaticity and conjugation," *J. Am. Chem. Soc.*, **99**, 444–450 (1979).
51. H. Dietrich, D. Bladauski, M. Grosse, K. Roth, and D. Rewicki, "Kristallstruktur und Reaktionen des 7*bH*-Indeno[1,2,3-*jk*]fluorens," *Chem. Ber.*, **108**, 1807 (1975).
52. H. W. Thompson, "The synthesis of triptindan," *J. Org. Chem.*, **33**, 621–625 (1968).
53. W. Ten Hoeve and H. Wynberg, "Synthetic approaches to planar carbon. 2," *J. Org. Chem.*, **45**, 2930–2937 (1980).
54. D. Kuck, "Single, double, and triple hydrogen rearrangement reactions in ionized 2-benzyl-1-indanols," *Adv. Mass Spectrom.*, **10**, 773–774 (1986).
55. W. Ten Hoeve and H. Wynberg, "Chiral spiranes. Optical activity and nuclear magnetic resonance spectroscopy as a proof for stable twist conformations," *J. Org. Chem.*, **44**, 1580–1514 (1979).
56. T. Prange, J. Drouin, F. Leyendecker, and J.-M. Conia, "X-Ray molecular structure of a highly symmetrical triketone: [3.3.3]Propellane-2,8,9-trione," *J. Chem. Soc. Chem. Commun.*, 430–431 (1977).
57. T. E. Bitterwolf, A. Ceccon, D. Kuck, et al., to be published.